FORM PTO-1390 (Modified) (REV 11-2000) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER: **215335US0XPCT**

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR): **09/926400**

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/JP00/02700	**25 April 2000**	**27 April 1999**

TITLE OF INVENTION
BACTERICIDAL ORGANIC POLYMERIC MATERIAL

APPLICANT(S) FOR DO/EO/US
Takanobu SUGO, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include itens (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☐ is attached hereto (required only if not communicated by the International Bureau).
   b. ☒ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☒ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

PC/IB/304 **Drawings (1 Sheet)**
PCT/IB/308
Notice of Priority
Request for Consideration of Documents Cited in the International Search Report

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
09/926400	PCT/JP00/02700	215335US0XPCT

24. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

		CALCULATIONS PTO USE ONLY
☐	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO	**$1040.00**
☒	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO	**$890.00**
☐	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	**$740.00**
☐	International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)	**$710.00**
☐	International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)	**$100.00**

ENTER APPROPRIATE BASIC FEE AMOUNT =	**$890.00**	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	**$130.00**	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	8 - 20 =	0	x $18.00	**$0.00**	
Independent claims	2 - 3 =	0	x $84.00	**$0.00**	
Multiple Dependent Claims **(check if applicable)**.			☐	**$0.00**	
TOTAL OF ABOVE CALCULATIONS =				**$1,020.00**	
☐ Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				**$0.00**	
SUBTOTAL =				**$1,020.00**	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +				**$0.00**	
TOTAL NATIONAL FEE =				**$1,020.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).** ☐				**$0.00**	
TOTAL FEES ENCLOSED =				**$1,020.00**	
				Amount to be: refunded	$
				charged	$

a. ☒ A check in the amount of **$1,020.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Telephone: (703)413-3000
Fax: (703)413-2220

Surinder Sachar
Registration No. 34,423

22850

Surinder Sachar
SIGNATURE

Norman F. Oblon
NAME

24,618
REGISTRATION NUMBER

Oct. 26 2001
DATE

215335US-0X PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :

TAKANOBU SUGO ET AL : ATTN: APPLICATION DIVISION

SERIAL NO: 09/926,400 :

FILED: OCTOBER 26, 2001 :

FOR: BACTERICIDAL ORGANIC POLYMERIC MATERIAL :

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Further to the Notification of Missing Requirements of November 30, 2001, Applicants submit the following Preliminary Amendment to the claims in the corrected English translation of the foreign application submitted concurrently herewith. Prior to examination on the merits, please amend the claims of the corrected English translation as follows.

IN THE CLAIMS

Please amend the claims as shown on the marked-up copy following this amendment to read as follows:

3. (Amended) The antimicrobial organic polymer material of Claim 1 wherein the unit derived from an N-alkyl-N-vinylalkylamide is derived from one or more polymerizable monomers selected from N-vinylpyrrolidone, 1-vinyl-2-piperidone, N-vinyl-N-

methylacetamide, N-vinyl-N-ethylacetamide, N-vinyl-N-methyl propylamide, N-vinyl-N-ethyl propylamide and derivatives thereof.

4. (Amended) The antimicrobial organic polymer material of Claim 1 wherein the polymer substrate is composed of a polyolefin-based organic polymer.

5. (Amended) The antimicrobial organic polymer material of Claim 1 in the form selected from a fiber, a woven/nonwoven fabric which is a fiber assembly and processed products thereof, fiber chips, beads, nets, films, plate members and bulk members.

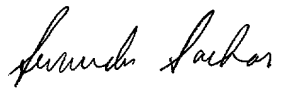
6. (Amended) An antimicrobial filter comprising the antimicrobial organic polymer material of Claim 1.

REMARKS

Claims 1-8 are active in the present application. Claims 3-6 have been amended to remove multiple dependencies. No new matter is added. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.



Norman F. Oblon
Attorney of Record
Registration No. 24,618

Stefan U. Koschmieder, Ph.D.
Registration No. 50,238

Surinder Sachar
Registration No. 34,423

22850

(703) 413-3000
Fax #: (703)413-2220
NFO:SUK\la
I:\atty\SUKOS\215335us-pr.wpd

Marked-Up Copy
Serial No: 09/926,400
Amendment Filed on:
1-30-2002

IN THE CLAIMS

Please amend the claims as follows:

--3. (Amended) The antimicrobial organic polymer material of Claim 1 [or 2] wherein the unit derived from an N-alkyl-N-vinylalkylamide is derived from one or more polymerizable monomers selected from N-vinylpyrrolidone, 1-vinyl-2-piperidone, N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide, N-vinyl-N-methyl propylamide, N-vinyl-N-ethyl propylamide and derivatives thereof.

4. (Amended) The antimicrobial organic polymer material of [any of Claims 1 to 3] Claim 1 wherein the polymer substrate is composed of a polyolefin-based organic polymer.

5. (Amended) The antimicrobial organic polymer material of [any one of Claims 1 to 4] Claim 1 in the form selected from a fiber, a woven/nonwoven fabric which is a fiber assembly and processed products thereof, fiber chips, beads, nets, films, plate members and bulk members.

6. (Amended) An antimicrobial filter comprising the antimicrobial organic polymer material of [any one of Claims 1 to 5] Claim 1.--

BACTERICIDAL ORGANIC POLYMERIC MATERIAL

FIELD OF THE INVENTION

The present invention relates to antimicrobial organic polymer materials capable of killing microorganisms, fungi, bacteria, viruses or the like in air or liquids.

PRIOR ART

Infectious diseases found in the medical field are known to often induce serious conditions and thought to be caused by antibiotic-resistant bacteria such as MRSA, VRSA and VRE or fungi, bacteria, viruses or the like. These are so-called nosocomial infections, which are not only contagious but also air-borne. Therefore, it is necessary to sterilize the outside air to be taken in or the inside air in closed spaces such as operating rooms, intensive care units or the like. The same problem occurs in closed spaces such as airplane cabins. A conventional means for sterilizing the air is an HEPA filter, which cannot be always an excellent sterilizing means because it suffers high air pressure losses and viruses pass through it and cannot be eliminated.

An object of the present invention is to solve these problems and to provide a filter material capable of killing microorganisms, fungi, bacteria, viruses or the like in the air or liquids.

DISCLOSURE OF THE INVENTION

It is well known that iodine has high antiseptic activity. For example, aqueous solutions of polyvinyl pyrrolidone carrying triiodide ion (povidone iodine) are widely used as antiseptics or mouth washers. However, povidone iodine shows high water solubility so that filter materials simply impregnated with this substance cannot serve as antimicrobial filters because the absorbed povidone iodine is totally released as soon as a liquid to be treated is passed through such filters. As a result of careful studies to provide a filter material fulfilling the above object by using this highly aseptic iodine, we accomplished the present invention on the basis of the finding that an antimicrobial organic polymer material capable of gradually releasing iodine molecules in triiodide ion into air or an aqueous medium to kill microorganisms can be provided by introducing a functional group capable of carrying triiodide ion (I_3^-) into a polymer side chain of an organic polymer material so that triiodide ion is carried on this polymer side chain via the functional group. As used herein, the term "antimicrobial" includes all of antimicrobial, antifungal, antibacterial, antiviral, etc.

Accordingly, the present invention relates to an antimicrobial organic polymer material comprising an organic polymer material having a polymer side chain containing a unit derived from an N-alkyl-N-vinylalkylamide on a backbone of a polymer substrate, wherein triiodide ion (I_3^-) is carried on said organic polymer material. As used herein, the expression "triiodide ion is carried" means

that triiodide ion and I_2 form a polyiodine to provide an adduct as counter ion to be carried on the polymer side chain.

N-alkyl-N-vinylalkylamides such as N-vinylpyrrolidone are widely known to bind to iodine as described above. However, no attempt has been so far made to provide an antimicrobial material having triiodide ion carried on said N-alkyl-N-vinylalkylamide group introduced in the form of a polymer side chain into a polymer substrate such as a resin or a nonwoven fabric.

Generally when a functional group is introduced into an organic polymer to confer a specific function, the backbones are crosslinked to each other to compensate for the deterioration of physical strength caused by the introduction of this functional group. Typical examples thereof are ion exchange resins, in which an ion exchange group such as a sulfone or quaternary ammonium group is generally introduced into a polystyrene backbone obtained by polymerizing a styrene monomer. However, these ion exchange groups are hydrophilic groups that are bulky by the surrounding several coordinated water molecules so that the resins are insufficient in physical strength and dissolve even in water. In order to solve this problem with ion exchange resins, polystyrene backbones are crosslinked to each other with a crosslinker such as divinylbenzene. This enhances physical strength of the resins, which no more dissolve in water, but the formation of a crosslinked structure impairs absorption/desorption

functions such as absorption speed or diffusion speed. This problem also occurs when an N-alkyl-N-vinylalkylamide is introduced into a backbone of an organic polymer substrate. That is, polymer materials cannot hold physical strength when an N-alkyl-N-vinylalkylamide group is directly introduced onto a polymer backbone, but their adsorption function is deteriorated if polymer backbones are crosslinked to each other for holding physical strength.

According to the present invention, it was found that an N-alkyl-N-vinylalkylamide group can be introduced into an organic polymer substrate while holding the physical strength of the polymer backbones by attaching a side chain in the form of a polymer chain containing a unit derived from the N-alkyl-N-vinylalkylamide onto a polymer backbone of the organic polymer substrate. The present invention will now be further explained in detail.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 schematically shows the antibacterial activity assay in the example of the present invention.

THE MOST PREFERRED EMBODIMENTS OF THE INVENTION

In antimicrobial organic polymer materials of the present invention, suitable means for introducing a side chain in the form of a polymer chain containing a unit derived from an N-alkyl-N-vinylalkylamide onto a backbone of an organic polymer substrate include graft polymerization. Especially, radiation-induced graft

polymerization is the most preferred method for the purpose of the present invention, because it is a method that permits a desired graft polymer side chain to be introduced into a polymer substrate by irradiating the substrate to produce a radical and reacting it with a graft monomer and characterized in that the number or length of the graft chain can be relatively freely controlled and the polymer side chain can be introduced into existing polymer materials in various shapes.

In the present invention, materials that can be used as substrates into which is introduced a side chain in the form of a polymer chain containing a unit derived from an N-alkyl-N-vinylalkylamide include woven and nonwoven fabrics composed of a polymer fiber or an assembly thereof. Woven/nonwoven fabric substrates are preferred materials for antimicrobial filters because they can be conveniently used as substrates for radiation-induced graft polymerization and are light and easy to process.

Radiations that can be used in radiation-induced graft polymerization well suitable for the purpose of the present invention include α-rays, β-rays, γ-rays, electron rays, UV ray, etc., among which γ-rays and electron rays are preferred for use in the present invention. Radiation-induced graft polymerization includes pre-irradiation graft polymerization involving preliminarily irradiating a graft substrate and then bringing it into contact with a polymerizable monomer (graft monomer) for reaction, and simultaneous irradiation graft polymerization involving

simultaneously irradiating a substrate and a monomer, both of which can be used in the present invention. Radiation-induced graft polymerization also includes various manners of contact between a monomer and a substrate, such as liquid phase graft polymerization performed with a substrate immersed in a monomer solution, gas phase graft polymerization performed with a substrate in contact with the vapor of a monomer, or immersion gas phase graft polymerization performed by immersing a substrate in a monomer solution and then removing it from the monomer solution for reaction in a gas phase, any of which can be used in the present invention.

Fiber or a woven/nonwoven fabric which is a fiber assembly is the most preferred materials for use as antimicrobial polymer materials of the present invention, and are well suitable for use in the immersion gas phase graft polymerization because they tend to retain monomer solutions.

Organic polymer substrates for antimicrobial polymer materials of the present invention are preferably polyolefin-based organic polymer materials. Polyolefin-based organic polymer materials are suitable for the purpose of introducing a graft side chain by radiation-induced graft polymerization because they are not disintegratable by radiation. When antimicrobial polymer materials of the present invention are used as filter materials, a fiber or a woven/nonwoven fabric which is a fiber assembly or processed products thereof are preferably

used as substrates.

In the present invention, a polymerizable monomer containing an N-alkyl-N-vinylalkylamide is graft polymerized on a backbone of an organic polymer substrate to prepare an organic polymer material having a polymer side chain containing a unit derived from the N-alkyl-N-vinylalkylamide on the backbone of the polymer substrate, and triiodide ion is carried thereon. Specific examples of compounds that can be used as polymerizable monomers for this purpose include one or more polymerizable monomers selected from N-vinylpyrrolidone, 1-vinyl-2-piperidone, N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide, N-vinyl-N-methyl propylamide, N-vinyl-N-ethyl propylamide and derivatives thereof.

Antimicrobial organic polymer materials of the present invention have a polymer side chain containing a unit derived from an N-alkyl-N-vinylalkylamide introduced onto a backbone of an organic polymer substrate, and triiodide ion (I_3^-) is carried on the N-alkyl-N-vinylalkylamide group present on this side chain, as described above.

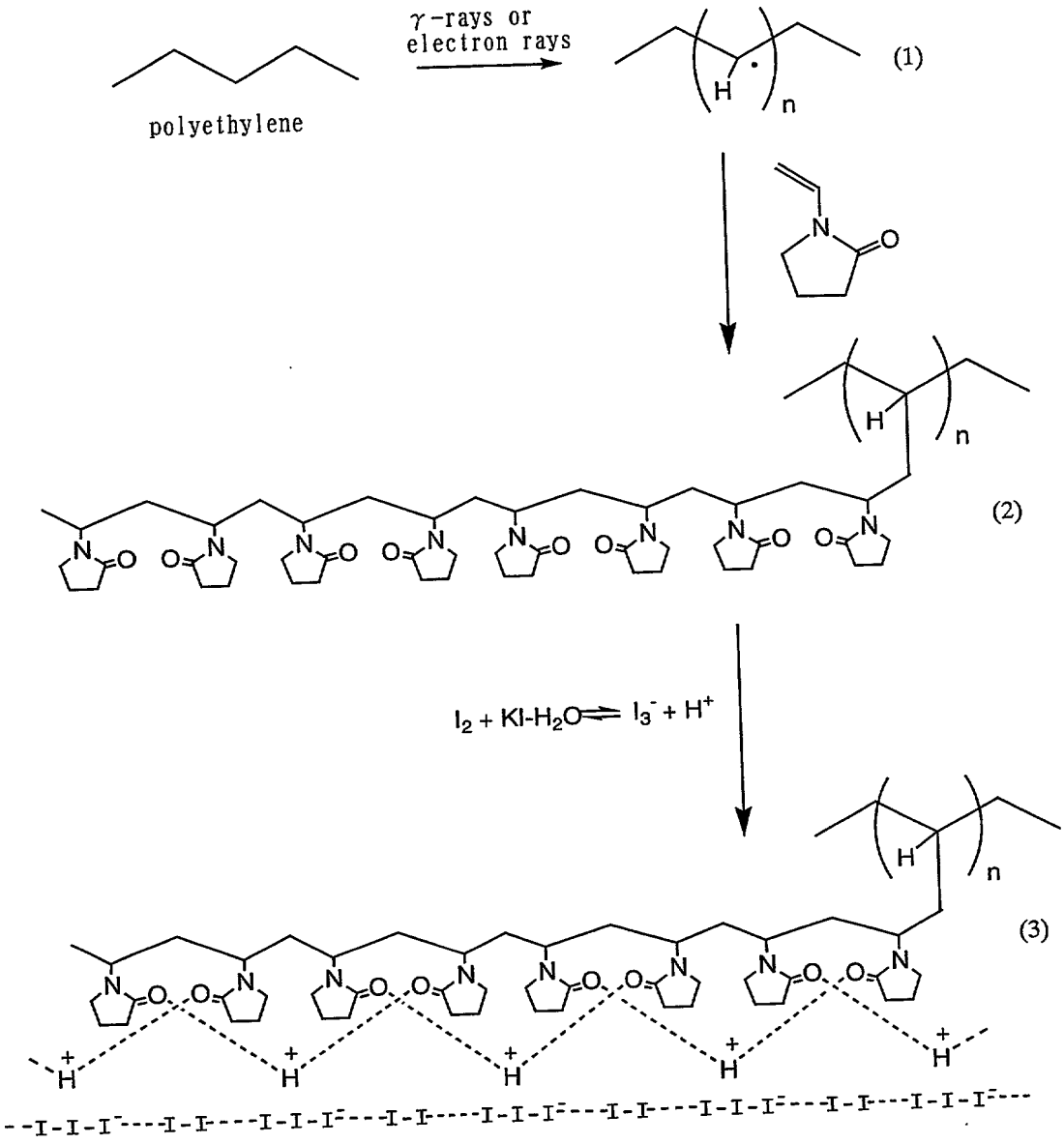
In order to load triiodide ion, an organic polymer material having a polymer side chain containing a unit derived from an N-alkyl-N-vinylalkylamide on a backbone of a polymer substrate as described above can be brought into contact with triiodide ion by immersing the polymer material in an aqueous iodine/potassium iodide solution or an aqueous iodine/hydrogen iodide solution or passing

said solution through a filter made of the polymer material, for example. Triiodide ion can also be carried on a polymer material by bringing the vapor of iodine into contact with the polymer material immersed in an aqueous iodine/potassium iodide solution or placing a similarly immersed polymer material on iodine powder and bringing the vapor of iodine emitted from the iodine powder into contact with the polymer material.

Triiodide ion can also be carried on a polymer material by immersing the polymer material in a solution of iodine dissolved in an organic solvent such as dichloromethane, chloroform or methanol, and adding hydroiodic acid to the solution.

The amount of triiodide ion to be carried on a polymer material varies with the nature of the medium to be sterilized, the amount of the microorganism to be eliminated such as bacteria, the operation environment of the polymer material, the shape of the polymer material, etc., but a preferred range is typically about 1-30% per unit weight of the polymer material.

As an example, a reaction for forming an antimicrobial polymer material of the present invention by graft polymerizing N-vinylpyrrolidone to a polymer substrate composed of a polyethylene nonwoven fabric via radiation-induced graft polymerization to form a polymer side chain containing a unit derived from N-vinylpyrrolidone and immersing said grafted polymer in an acidic iodine/potassium iodide solution seems to proceed as shown below.

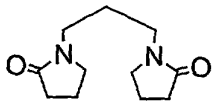


In order to explain the above structure, we prepared a dimer of N-vinylpyrrolidone (represented by formula (4) below) and determined the resonance Raman spectrum of a compound (represented by formula (5) below) obtained by reacting said dimer with an acidic iodine/potassium iodide solution, which showed absorption of I_3^- at 107.7 cm^{-1}. The

X-ray crystal structure analysis of the resulting compound showed that it has a structure containing intermolecular hydrogen bonds as shown in formula (5) below but not intramolecular hydrogen bonds. This was also proved by the molecular orbital calculation using PM3 hamiltonian showing that intermolecular hydrogen bonds are more stable than intramolecular hydrogen bonds. This result shows that no hydrogen bond occurs between adjacent pyrollidone units in the compound of formula (3) above. The resonance Raman spectrum of compound (3) prepared according to the scheme shown above showed absorption of I_3^- at 110.7 cm^{-1} and absorption of I_2 at 166.7 cm^{-1}. These results proved that triiodide ion I_3^- is combined with iodine I_2 to form a polyiodine:

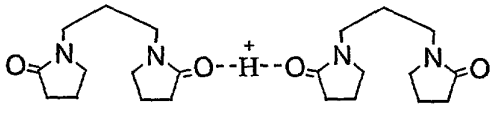
... I_3^- ... I_2 ... I_3^- ... I_2 ...

which provides a counter ion adduct carried on antimicrobial polymer materials of the present invention as shown in formula (3) above.



(4)

$I_2 + KI\text{-}H_2O \rightleftharpoons I_3^- + H^+$



(5)

I-I-I$^-$

Antimicrobial polymer materials of the present invention have triiodide ion in the form of a polyiodine carried on a polymer side chain containing a unit derived from an N-alkyl-N-vinylalkylamide present on a backbone of a polymer substrate as described above, so that if such materials are used as filters for liquid through which a liquid to be treated containing bacteria or viruses is passed, iodine (I_2) is liberated from the polyiodine carried on the filters to kill the bacteria or viruses in the liquid to be treated and iodine in the polyiodine adduct gradually dissolves into the liquid to be treated to further kill the bacteria or viruses in the liquid to be treated. Antimicrobial polymer materials of the present invention can hold high antimicrobial activity for a long period because triiodide ion is carried as counter ion in the form of a polyiodine with iodine (I_2) as shown in the scheme above and thus slowly released. If antimicrobial polymer materials of the present invention are used as gas filters, iodine in the carried triiodide ion evaporates and diffuses in the gas to be treated to sterilize the gas to be treated. In this case, antimicrobial polymer materials of the present invention can also hold high antimicrobial activity for a long period because iodine shows slow-release characteristics.

Polymer materials carrying triiodide ion shows the color of iodine, which gradually fades as iodine is released. Thus, the carried amount of the remaining iodine, i.e., the remaining antimicrobial activity of antimicrobial

polymer materials can be evaluated by the color density of the antimicrobial polymer materials. Taking advantage of this phenomenon, antimicrobial polymer materials of the present invention can be optically monitored for their antimicrobial activity. Monitoring can be made by visual observation or by measuring the absorption/reflection of iodine in the visible light range using a spectrophotometer. For example, antimicrobial polymer materials of the present invention can be considered to have consumed antimicrobial activity and replaced by fresh one or regenerated when they almost lose the color of iodine. The color density at which sufficient antimicrobial activity cannot be shown can be experimentally determined depending on various parameters such as the amount of iodine carried on the antimicrobial material, the shape or size of the antimicrobial material, conditions of the liquid or gas to be treated with the antimicrobial material, etc.

When antimicrobial polymer materials of the present invention can show no more sufficient antimicrobial activity after iodine in triiodide ion carried in the form of a polyiodine adduct is released, they can be conveniently regenerated by reloading triiodide ion on the antimicrobial polymer materials. Reloading of triiodide ion for regeneration can be performed in the same manner as for the preparation of antimicrobial polymer materials.

Antimicrobial polymer materials of the present invention can be in any of various shapes such as a woven/nonwoven fabric, plate member, bead member, bulk

member, film, net or the like.

Antimicrobial polymer materials of the present invention can be used to sterilize any medium susceptible to the presence of microorganisms, bacteria or the like. For example, antimicrobial polymer materials of the present invention can be formed into a nonwoven fabric and used as air filters for sterilization/disinfection such as air filters for air-conditioners in hospitals, air filters for green houses, filters for safety cabinets or air filters for air-conditioning airplane cabins; antibacterial/antiviral filters for agricultural water, waste liquor, cooling tower water or sewage treatment plant water; water filters in culture ponds; filters for circulation bath tabs; or bandages or medical absorbent gauzes or masks. Antimicrobial polymer materials of the present invention can also be used in fumigation treatments by covering the soil with said materials in the form of a sheet or mixing said materials in the form of fiber chips into the soil.

As described above, antimicrobial organic polymer materials of the present invention comprise a polymer material having a polymer side chain containing at least a unit derived from an N-alkyl-N-vinylalkylamide on a backbone of a polymer substrate, wherein triiodide ion is carried in the form of a polyiodine on said polymer material, and they are very useful as antimicrobial materials for the air or liquids because they have high physical strength and can gradually release iodine in the

triiodide ion carried in the form of a polyiodine. Antimicrobial organic polymer materials of the present invention lose their color as iodine in the carried triiodide ion is released, so that their remaining antimicrobial activity can be monitored by the color of the materials. In addition, their antimicrobial activity can be very conveniently regenerated by reloading triiodide ion when it has been consumed.

INDUSTRIAL APPLICABILITY

Antimicrobial organic polymer materials of the present invention are very useful as antimicrobial materials for use in environments susceptible to the presence of microorganisms or bacteria such as air filters for air-conditioners in hospitals, antibacterial/antiviral filters for agricultural water or filters for circulation bath tabs or water filters for culture ponds. Especially, they can be sufficiently applied to causal agents for nosocomial infections among recent issues such as MRSA, VRSA, VRE.

EXAMPLES

The following examples further illustrate the present invention without, however, limiting the same thereto.

Example 1: Preparation of an antimicrobial polymer material

A nonwoven fabric having an areal density of 56 g/m^2 and a thickness of 0.2 mm which has been made of a polyethylene fiber of about 16 μm in diameter was used as a

polymer substrate. This nonwoven fabric substrate was irradiated with γ-rays at 150 kGy in a nitrogen atmosphere and then immersed in an N-vinylpyrrolidone solution, which was heated for reaction to give an N-vinylpyrrolidone-grafted nonwoven fabric at a grafting degree of 134%. This grafted nonwoven fabric was cut into 15 cm x 5 cm (0.1984 g in weight), thoroughly immersed in pure water and lightly drained, and then stirred for 1 hour in a mixed solution of 10 ml of 0.1 N iodine/potassium iodide solution or 0.1 N iodine/hydrogen iodide solution plus 190 ml of pure water. Then, it was immersed in 20 ml of 1 N hydrochloric acid solution for 10 minutes, and then washed with water, and the immersion solution of hydrochloric acid and the washing water were combined and titrated with 0.1 N Na_2SO_3 to assay the amount of iodine remaining in the solution, whereby the amount of iodine adsorbed to the nonwoven fabric material was determined. The resulting nonwoven fabric sample was dried and weighed (0.2725 g). The loading level of triiodide ion (I_3^-) was 1.40 mmol.

Example 2: Antibacterial activity assay

Test pieces in the form of a circle of 13 mm in diameter were stamped out from the nonwoven antimicrobial material prepared in Example 1. The strains tested were Micrococcus luteus ATCC 9341, Bacillus anthracis and Escherichia coli NIHJ. These strains maintained on slants were cultured on nutrient broth for 8 hours. The resulting cultures were partially collected and further cultured on

nutrient broth for 18 hours. A dish was prepared containing 7 ml of nutrient agar sterilized by autoclaving and solidified. Nutrient broth containing 0.8% agar was sterilized by autoclaving and cooled to about 50°C, and 7 ml of this medium was mixed with each test strain cultured as above at a density of about 5×10^6 cells/ml and uniformly spread and solidified on said nutrient agar dish to prepare a plate, on which the test piece was placed and lightly pressed. As control samples, the polyethylene nonwoven fabric was cut into the same size as that of the test piece and placed on a similar plate without treatment or after impregnation with a polyvinyl pyrrolidone/iodine (povidone iodine) solution or an aqueous potassium iodide solution (0.05 mmol/l), and lightly pressed. The plate alone was also tested for confirming the growth of the strain.

Thus prepared plate samples were incubated for 24 hours in an incubator kept at 37°C. The diameter L (mm) of the growth inhibition circle formed around each test piece was measured. The inhibition circle width was calculated by the equation below:

$$W = (L - T) / 2$$

where W = inhibition circle width; L = inhibition circle diameter (mm); T = test piece diameter (mm).

The inhibition circle width was the average of triplicate measurements on each test strain. Table 1 shows test results of the antimicrobial material of the present invention and Table 2 shows test results of control samples.

Fig. 1 schematically shows the assay.

It was observed from Table 1 that the antimicrobial material of the present invention shows good antibacterial activity against each test strain. Said material kept the color of iodine after evaluation, i.e., iodine was not totally released during the test period of 24 hours, showing that it can be repeatedly used. No inhibition circle appeared in the control sample of an untreated polyethylene nonwoven fabric. The polyethylene nonwoven fabric impregnated with a povidone iodine solution and the polyethylene nonwoven fabric impregnated with an aqueous potassium iodide solution (0.05 mmol/l) totally lost the color of iodine and could not be repeatedly used though they showed antibacterial activity. The inhibition circle widths of these control samples were much smaller than that of the present invention, probably because the impregnated iodine was very rapidly released and evaporated and lost during the test period of 24 hours.

Example 3: Antifungal activity assay

The test strain was Candida albicans 3143. The strain maintained on slants was cultured on nutrient broth for 8 hours. The resulting cultures were partially collected and further cultured on nutrient broth for 18 hours. A dish was prepared containing 7 ml of nutrient agar sterilized by autoclaving and solidified. Complete medium for fungi containing 0.8% agar was sterilized by autoclaving and cooled to about 50°C, and 7 ml of this medium was mixed

with the test strain cultured as above at a density of about 5 x 10^6 cells/ml and uniformly spread and solidified on said nutrient agar dish to prepare a plate, on which the test piece was placed and lightly pressed. As a control sample, the polyethylene nonwoven fabric was cut into the same size as that of the test piece and placed on a similar plate and lightly pressed. The plate alone was also tested for confirming the growth of the strain. The plate samples were incubated for 24 hours in an incubator to calculate the width of the growth inhibition circle in the same manner as in Example 2. The results are shown in Table 1

It was observed from Table 1 that the antimicrobial material of the present invention shows good antifungal activity. Said material kept the color of iodine after evaluation, i.e., triiodide ion was not totally released during the test period of 24 hours, showing that it can be repeatedly used. No inhibition circle appeared in the polyethylene nonwoven fabric and the plate alone (control samples).

Table 1

	Antibacterial activity			Antifungal activity
Strain	Micrococcus luteus ATCC 9341	Bacillus anthracis	E.coli NIHJ	Candida albicans
Cell density (cells/ml)	5.0×10^6	5.0×10^6	5.0×10^6	5.0×10^6
Inhibition circle width (mm)	14.8 ± 0.3	18.0 ± 3.1	12.8 ± 1.8	3.7 ± 0.5
Note:	Test piece diameter = 13 mm			

Table 2: Control test results

	Antibacterial activity		
Test material	Poly-ethylene	Polyethylene + PVP/I_2	Polyethylene + iodine solution (0.05 mmol/l)
Cell density (cells/ml)	5.0×10^6	5.0×10^6	5.0×10^6
Inhibition circle width (mm)	0	0.92 ± 0.14	1.58 ± 0.52
Note:	Test piece diameter = 13 mm; Test strain = Micrococcus luteus ATCC 9341		

CLAIMS

1. An antimicrobial organic polymer material comprising an organic polymer material having a polymer side chain containing a unit derived from an N-alkyl-N-vinylalkylamide on a backbone of a polymer substrate, wherein triiodide ion is carried on said organic polymer material.

2. The antimicrobial organic polymer material of Claim 1 wherein the polymer side chain containing a unit derived from an N-alkyl-N-vinylalkylamide has been introduced onto a backbone of a polymer substrate by radiation-induced graft polymerization.

3. The antimicrobial organic polymer material of Claim 1 or 2 wherein the unit derived from an N-alkyl-N-vinylalkylamide is derived from one or more polymerizable monomers selected from N-vinylpyrrolidone, 1-vinyl-2-piperidone, N-vinyl-N-methylacetamide, N-vinyl-N-ethylacetamide, N-vinyl-N-methyl propylamide, N-vinyl-N-ethyl propylamide and derivatives thereof.

4. The antimicrobial organic polymer material of any one of Claims 1 to 3 wherein the polymer substrate is composed of a polyolefin-based organic polymer.

5. The antimicrobial organic polymer material of any one of Claims 1 to 4 in the form selected from a fiber, a woven/nonwoven fabric which is a fiber assembly and processed products thereof, fiber chips, beads, nets, films, plate members and bulk members.

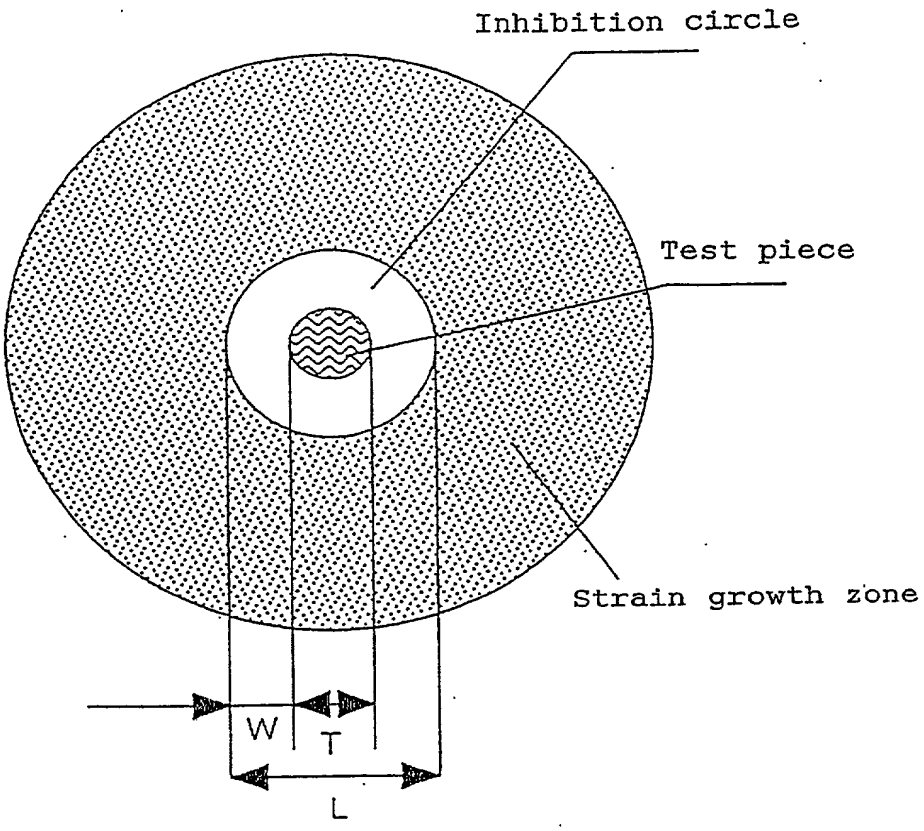
6. An antimicrobial filter comprising the antimicrobial

organic polymer material of any one of Claims 1 to 5.

7. A process for preparing an antimicrobial organic polymer material, comprising introducing a polymer side chain containing a unit derived from an N-alkyl-N-vinylalkylamide onto a backbone of an organic polymer substrate and loading triiodide ion on the resulting polymer material.

8. The process of Claim 7 wherein the polymer side chain containing a unit derived from an N-alkyl-N-vinylalkylamide is formed by graft-polymerizing a polymerizable monomer containing an N-alkyl-N-vinylalkylamide onto a backbone of a polymer substrate via radiation-induced graft polymerization.

Fig. 1



W: Inhibition circle width

L: Inhibition circle diameter

T: Test piece diameter

Declaration and Power of Attorney For Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name.

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者（下記の名称が複数の場合）であると信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

BACTERICIDAL ORGANIC POLYMERIC MATERIAL

上記発明の明細書は、

the specification of which

☐ 本書に添付されています。

☐ is attached hereto.

☒ ___月___日に提出され、米国出願番号または特許協定条約国際出願番号を_____とし、
（該当する場合）_____に訂正されました。

☒ was filed on April 25, 2000
as United States Application Number or
PCT International Application Number
PCT/JP00/02700 and was amended on
_____ (if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

Japanese Language Declaration
(日本語宣言書)

私は、米国法典第35編119条（a）-（d）項又は365条（b）項に基づき下記の、米国以外の国の少なくとも一ヵ国を指定している特許協力条約365（a）項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)
外国での先行出願

(Number) (番号)	(Country) (国名)	(Day/Month/Year Filed) (出願年月日)	Priority Claimed 優先権主張 Yes はい	No いいえ
119200/1999	Japan	27/4/1999	☒	☐
			☐	☐

私は、第35編米国法典119条（e）項に基づいて下記の米国特許出願規定に記載された権利をここに主張いたします。

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.) (出願番号)	(Filing Date) (出願日)

私は、下記の米国法典第35編120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約365条（c）に基づく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国際提出日までの期間中に入手された、連邦規則法典第37編1条56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

(Application No.) (出願番号)	(Filing Date) (出願日)	(Status: Patented, Pending, Abandoned) (現況：特許許可済、係属中、放棄済)

私は、私自信の知識に基づいて本宣言書中で私が行なう表明が真実であり、かつ私の入手した情報と私の信じるところに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行なえば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Japanese Language Declaration
(日本語宣言書)

委任状：私は下記の発明者として、本出願に関する一切の手続きを米特許商標局に対して遂行する弁理士または代理人として、下記の者を指名いたします。
(弁護士、または代理人の指名及び登録番号を明記のこと)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: *(list name and registration number)*

022850

書類送付先

Send Correspondence to:

022850

直接電話連絡先：（名前及び電話番号）

Direct Telephone Calls to: (name and telephone number)

(703) 413-3000

単独発明者または第一の共同発明者の氏名	Full name of sole or first joint inventor Takanobu SUGO
発明者の署名　日付	Inventor's signature　Date Takanobu Sugo　Oct. 30, 2001
住所	Residence Gunma, Japan　JPX
国籍	Citizenship Japanese
郵便の宛先	Post Office Address c/o Japan Atomic Energy Research Institute, Takasaki Radiation
	Chemistry Research Establishment of 1233 Watanuki-cho, Takasaki-shi, Gunma 370-1292 Japan
第二の共同発明者の氏名	Full name of second joint inventor, if any Kazuyoshi TAKEDA
第二の共同発明者の署名　日付	Second joint Inventor's signature　Date Kazuyoshi Takeda　Oct. 30, 2001
住所	Residence Kanagawa, Japan　JPX
国籍	Citizenship Japanese
郵便の宛先	Post Office Address c/o Ebara Research Co., Ltd. of
	4-2-1, Honfujisawa, Fujisawa-shi, Kanagawa 251-8502 Japan

(第三以降の共同発明者についても同様に記載し、署名すること)

(Supply similar information and signature for third and subsequent joint inventors.)

Japanese Language Declaration
(日本語宣言書)

第三の共同発明者の氏名	Full name of third joint inventor, if any Kunio FUJIWARA
第三の共同発明者の署名　日付	Third joint Inventor's signature Kunio Fujiwara　Date Oct. 30, 2001
住所	Residence Kanagawa, Japan　JPX
国籍	Citizenship Japanese
郵便の宛先	Post Office Address c/o Ebara Research Co, Ltd. of 4-2-1, Honfujisawa, Fujisawa-shi, Kanagawa 251-8502 Japan

第四の共同発明者の氏名	Full name of fourth joint inventor, if any Tadashi ADACHI
第四の共同発明者の署名　日付	Fourth joint Inventor's signature Tadashi Adachi　Date Oct. 30, 2001
住所	Residence Tokyo, Japan　JPX
国籍	Citizenship Japanese
郵便の宛先	Post Office Address c/o Ebara Corporation of 11-1, Haneda Asahi-cho, Ohta-ku, Tokyo 144-8510 Japan

第五の共同発明者の氏名	Full name of fifth joint inventor, if any Hideo KAWAZU
第五の共同発明者の署名　日付	Fifth joint Inventor's signature Hideo Kawazu　Date Oct. 30, 2001
住所	Residence Kanagawa, Japan　JPX
国籍	Citizenship Japanese
郵便の宛先	Post Office Address c/o Ebara Research Co, Ltd. of 4-2-1, Honfujisawa, Fujisawa-shi, Kanagawa 251-8502 Japan

第六の共同発明者の氏名	Full name of sixth joint inventor, if any Makoto KOMATSU
第六の共同発明者の署名　日付	Sixth joint Inventor's signature Makoto Komatsu　Date Oct. 30, 2001
住所	Residence Kanagawa, Japan　JPX
国籍	Citizenship Japanese
郵便の宛先	Post Office Address c/o Ebara Research Co, Ltd. of 4-2-1, Honfujisawa, Fujisawa-shi, Kanagawa 251-8502 Japan

(第六またはそれ以降の共同発明者に対しても同様な情報および署名を提供すること。)

(Supply similar information and signature for third and subsequent joint inventors.)

Japanese Language Declaration
(日本語宣言書)

第七の共同発明者の氏名	Full name of seventh joint inventor, if any Junichi KANNO
第七の共同発明者の署名 日付	7th joint Inventor's signature Date Junichi Kanno Oct. 30, 2001
住所	Residence Kanagawa, Japan JPX
国籍	Citizenship Japanese
郵便の宛先	Post Office Address c/o Ebara Research Co, Ltd. of 4-2-1, Honfujisawa, Fujisawa-shi, Kanagawa 251-8502 Japan

第八の共同発明者の氏名	Full name of eighth joint inventor, if any Takeshi TAKAI
第八の共同発明者の署名 日付	8th joint Inventor's signature Date Takeshi Takai Oct. 30, 2001
住所	Residence Kanagawa, Japan JPX
国籍	Citizenship Japanese
郵便の宛先	Post Office Address c/o Ebara Research Co, Ltd. of 4-2-1, Honfujisawa, Fujisawa-shi, Kanagawa 251-8502 Japan

第九の共同発明者の氏名	Full name of ninth joint inventor, if any
第九の共同発明者の署名 日付	9th joint Inventor's signature Date
住所	Residence
国籍	Citizenship
郵便の宛先	Post Office Address

第十の共同発明者の氏名	Full name of tenth joint inventor, if any
第十の共同発明者の署名 日付	10th joint Inventor's signature Date
住所	Residence
国籍	Citizenship
郵便の宛先	Post Office Address

(第六またはそれ以降の共同発明者に対しても同様な情報および署名を提供すること。)

(Supply similar information and signature for third and subsequent joint inventors.)